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Preliminary communication

Azole chemistry
VII*. The effect of metal complexation on a ring–chain tautomeric equilibrium

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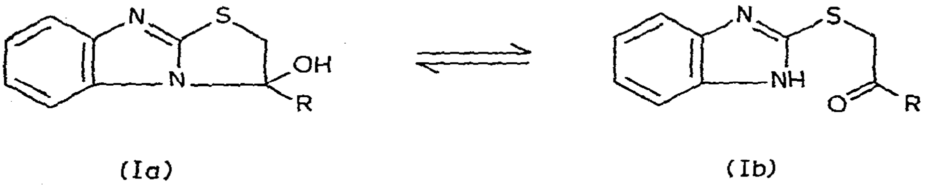
SUMMARY

The chromium tricarbonyl group significantly affects the position of an oxazolidine–imino alcohol tautomeric equilibrium.

Dynamic ring–chain tautomerism [e.g. Ia ⇌ Ib] has been encountered in a wide variety of heterocyclic systems[2]. Although a number of studies have been carried out in order to gain some insight as to the factors [e.g. inductive, resonance, etc.] which affect the tautomeric equilibrium[2], there have been no publications on the effect of metal complexation on the ring-chain process. This communication reports the first example of such an effect.



We had hoped to prepare I, $R = CH_3$, having a chromium tricarbonyl group complexed to the benzene ring. Unfortunately, only n-donor ligand complexes were isolated from the reaction of I, $R = CH_3$, with chromium hexacarbonyl in di-n-butyl ether.

The synthesis of a complexed oxazolidine, which can exist in equilibrium with its imino alcohol chain tautomer[3], proved more fruitful. When an equimolar mixture of

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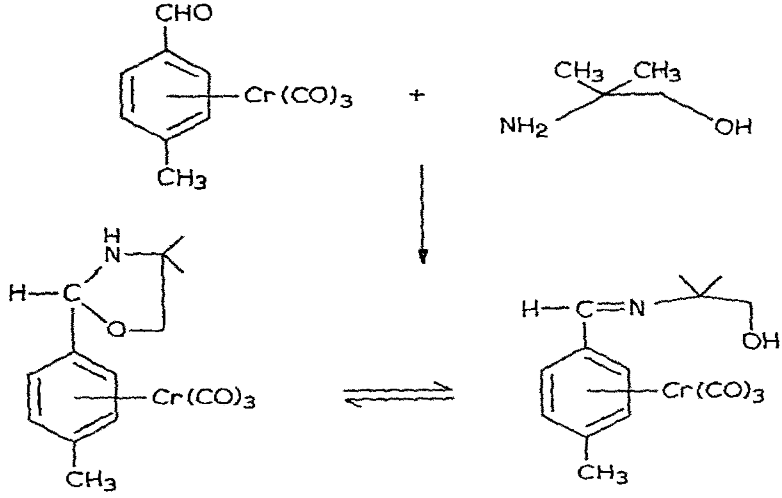
* For Part VI, see ref. 1.

p-tolualdehyde chromium tricarbonyl[4] and 2-amino-2-methyl-1-propanol (in dry tetrahydrofuran) were stirred at room temperature for 6 h over 4Å molecular sieves, the yellow-orange complex II was obtained in 68% yield [Found: C, 55.21; H, 5.17; N, 4.01; Cr, 15.43. $C_{15}H_{17}NO_4Cr$ calcd.: C, 55.04; H, 5.24; N, 4.28; Cr, 15.89%]. Terminal metal carbonyl stretching bands appeared in the infrared at 1958 and 1875 cm^{-1} while the imine stretching vibration [of IIb] occurred at 1635 cm^{-1}. A molecular ion peak was observed in the mass spectrum at *m/e* 327, followed by successive loss of three carbonyls [also fragments at *m/e* $91(C_7H_7)^+$, $52(Cr)^+$].



(IIa) (IIb)

The nuclear magnetic resonance spectrum [CCl_4, 5 mole %] indicated the presence of IIa and its chain isomer IIb in the ratio of 4.3/1.0. The ratio was determined by integration of the signal for the methine proton of IIb [δ 7.75], and the signals for the methine proton of IIa as well as those for the aromatic protons of IIa and IIb which all occur in the region of δ 5.04–6.10. A ratio of 1.22/1.00 was obtained for uncomplexed IIa/IIb, in reasonable accord with previously published data[3]. Therefore, the chromium tricarbonyl group has significantly affected the position of the tautomeric equilibrium.

A ratio of approximately 4.6/1.0 was determined for IIa/IIb containing a *p*-nitro rather than a *p*-methyl substituent, but no $Cr(CO_3)$ group [based on the data in reference 3]. Since a methyl group is electron-donating, it is reasonable to expect a modest increase in the proportion of chain tautomer for IIa/IIb as compared to the analogous complex having hydrogen in the *para* position. Earlier work has indicated that the chromium tricarbonyl group is inductively similar to a *p*-nitro group[5], and the same conclusion can be drawn from the results obtained herein [although resonance effects on IIb must contribute to some extent].

ACKNOWLEDGMENT

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REFERENCES

1 H. Alper and R.W. Stout, *J. Heterocyclic Chem.*, in press.
2 H. Alper, E.C.H. Keung and (in part) R.A. Partis, *J. Org. Chem.*, 36 (1971) 1352 and references cited therein.
3 J.V. Paukstelis and L.L. Lambing, *Tetrahedron Lett.*, (1970) 299.
4 H.P. Fritz and C.G. Kreiter, *J. Organometal. Chem.*, 7 (1967) 427.
5 *E.g.*, B. Nicholls and M.C. Whiting, *J. Chem. Soc.*, (1959) 551; G. Klopman and F. Calderazzo, *Inorg. Chem.*, 6 (1967) 977; G. Klopman and K. Noack, *Inorg. Chem.*, 7 (1968) 579; R.S. Bly and R.L. Veazey, *J. Amer. Chem. Soc.*, 91 (1969) 4221; R.S. Bly, R.C. Strickland, R.T. Swindell and R.L. Veazey, *J. Amer. Chem. Soc.*, 92 (1970) 3722; A. Ceccon and G.S. Biserni, *J. Organometal. Chem.*, 39 (1972) 313.